NITROGEN TYPES IN LIGHT DISTILLATES FROM ABOVEGROUND AND IN SITU COMBUSTION PRODUCED SHALE OILS

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INTRODUCTION

There is some evidence that in situ retorted shale oils may have generally lower hetero-atom and polar compound concentrations than aboveground retorted oils.[1,2] This could make in situ oils more attractive as refinery feedstock or as fuel sources than oboveground produced oils. To help determine if differences in heterocompound composition might exist between oils produced in these different ways, light distillate fractions (400° to 600° F nominal boiling range) from two different types of internal combustion retorting processes, one aboveground and one in situ, were compared in analyses. Both oils were produced in forward-burn type pracesses in which the exiting oil had the opportunity for contacting raw oil shale or included minerals.

The main difference in the two retorting processes was the time–temperature history of the oils produced. The aboveground process using crushed shale was a rapid–heat, high temperature process whereas the in situ process was apparently a slow–heat, low temperature process.[1] Direct gas-to-solids heat exchange occurs in both processes. Other imponderables such as the contact of the product oil with raw shale or air in either case, or raw or spent shale in situ could, of course, affect the character of the oil also.

The aboveground retorted oil (AGRO) was made from a shale oil produced from Colorado Green River Formation oil shale by the Union Oil Retort A[3] and its nitrogen bases have been studied before.[4]

Additional compound-type information is available from early work with a shale-oil naph-tha[5] and a heavy gas oil[6] from a different aboveground combustion retort-produced crude (a Nevada-Texas-Utah type retort). Much of this compound-type information has been drawn upon in the following discussion when specific compound types are postulated as relating to a nitrogen- or oxygen-type value determined.

The in situ retorted oil (ISRO) studied here was made from a shale oil produced in the Northern Green River Formation near Rock Springs, Wyoming.[7] The shale used in the aboveground retort came from the Mahogany zone of the Piceance Basin in Colorado. Although the oil shales used were far apart, they were both of the Green River Formation. The Wyoming shale appears to be very similar in composition and properties to the extensively studied Mahogany zone oil shales.[8] Therefore, it was assumed that if both shales had been retorted in the same way, the oils produced would have been similar.

The light distillate from the aboveground retorted oil (AGRO) represents 15 percent of the crude, but the light distillate from the in situ retorted oil (ISRO) represents 50 percent of the crude. A larger proportion of light products appears to be characteristic of in situ-produced shale oils.[1] In table 1 the heteroatomic concentrations are shown for the two distillates. Both oils have similar nitrogen levels, but sulfur and oxygen are much lower in the ISRO. The nature of sulfur and oxygen compounds in shale oils has been summarized earlier[9] and in this symposium.[2] For production of refined products, sulfur and oxygen compound types apparently disappear with

hydrodenitrogenation before nitrogen types so that the nitrogen-type assessment seems of primary importance. For other contemplated uses of the resource, such as low grade burner fuel or as a source of specific chemical compounds, other heteroatomic compounds could be of comparable importance.

TABLE 1. – Heterootoms in the shale-oil light distillates (400° to 600° F)

Element	Aboveground retorted oil	In situ retorted oil
	A	B
Total nitrogen	1.34	1.34
Sulfur	.90	.53
Oxygen (by difference in ultimate onalysis)	1.24	.35

The weight-overage molecular weight for the oils corresponds to $C_{14.3}$ or 200 based on simulated distillotion. Using this value and assuming, for illustration, a maximum of heterocompounds with one nitrogen atom per molecule, the nitrogen levels shown in toble 1 would represent 20 percent nitrogen-type compounds in either distillate. With similar assumptions for oxygen and sulfur, the AGRO would contain about 16 percent oxygen compounds ond 6 percent sulfur compounds. The ISRO distillate would contain obaut 4 percent oxygen compounds ond 3 percent sulfur compounds. Over 80 percent of the nitrogen in either of these oils is titratable os basic compounds.

This poper reports a comparison of some observed nitrogen types in these two oils (distillates). In addition, some oxygen types have been estimated because they oppear to relate closely to the chemistry of the nitrogen types ond there is a lorge difference in the elemental oxygen contents of the oils. Techniques for nitrogen-type characterizotion of shole oils developed and applied previously[4,10] have been used. Some techniques in a state of development for phenolic and carboxylic acid-type characterization of shale oils have been applied also.

EXPERIMENTAL WORK

Separation Procedure

The fractionation scheme used is depicted in detail in figure 1 and summarized in table 2. The procedure[11] involved anion-exchange fractionation followed by cation-exchange fractionation to prepare three acid fractions (A_1, A_2, A_3) and three base fractions (B_1, B_2, B_3). The raffinate from this procedure was further fractionated on a ferric chloride-Attapulgus clay column[11] into three fractions (N_0, N_1, and N_2). The first of these neutral fractions, N_0, is referred to also as the HC (hydrocarbon) fraction. Approximately 50 g of each distillate was fractionated using 50 g of each ion-exchange resin. Twenty grams of the raffinate from the ion-exchange resins was separated on 140 g of the ferric chloride-Attapulgus clay mixture.

The solvents were percolated at 20° C through the column removing most of the material in the fraction. The remaining amount of material was removed by percolating fresh solvent through the column and recirculating by distillation the solvent from the receiver back to the top of the column. Percolation was continued until there was no evidence of sample being desorbed from the column. Solvents were removed at reduced pressure, with slight rectification, and the recovered fractions were stored under an inert atmosphere at 0° C.
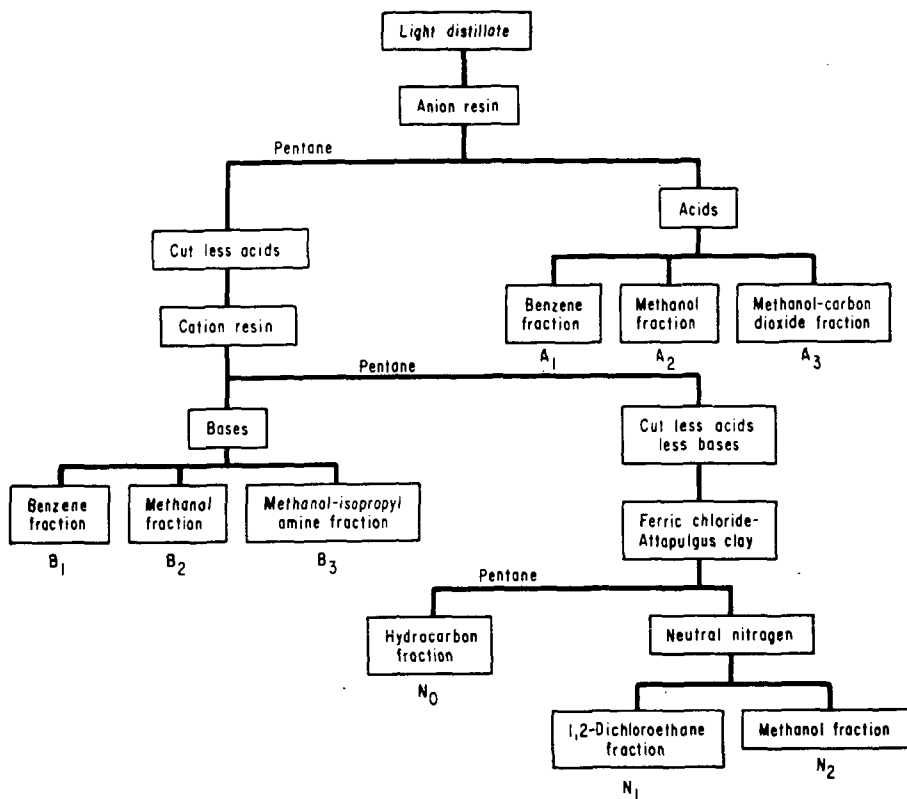
FIGURE 1. - Separation scheme.

Reagents

Adsorbents

The anion- and cation-exchange resins were Rohm and Haas Amberlyst A-29 and Amberlyst A-15, respectively. The resins and ferric chloride supported on clay were prepared, activated, and extracted as described by Jewell.[11]

Solvents

N-pentane (99 percent, Phillips Petroleum) was purified by percolation through activated silica gel and by flash distillation. Benzene and methanol (reagent grade, J. T. Baker) were flash distilled as was 1,2-dichloroethane (Eastman Chemical Co.). The isopropyl amine (reagent grade, Eastman) was used as received. Acetonitrile and dioxane used in the titrations were purified by passing through activated alumina.

TABLE 2. – Anion-, cation-exchange, and ferric chloride–Attapulgus clay
fractionation sequence

Fraction name	Desorbing solvent	Amount, wt-pct of distillate	
		Aboveground combustion retorted oil[a]	In situ combustion retorted oil[b]
Acids From Anion-Exchange			
Resin Column			
A_1, very weak	Benzene	1.65	1.32
A_2, very weak	Methanol	1.60	1.87
A_3, weak	Methanol–carbon dioxide	1.32	.76
Bases From Cation-Exchange			
Resin Column			
B_1, very weak	Benzene	.48	.57
B_2, very weak	Methanol	.11	.08
B_3, weak	Methanol–isopropylamine	8.45	10.12
Neutrals From Ferric Chloride			
Clay Column			
N_0 hydrocarbon	Pentane	79.44	81.85
N_1 first neutral	1,2-Dichloroethane	4.75	2.84
N_2 second neutral	Methanol	2.20	.63

[a] 2.6 Percent loss apportioned throughout.
[b] 1.6 Percent loss apportioned throughout.

Characterization Procedures

Procedures applied to shale oil previously have been described earlier[4,10,12-19] but will be summarized here along with procedures for oxygen types being developed. The sequence in the separation scheme is a potent characterization tool in itself and is used to supplement information obtained from more direct determinations described below. The various fractions have been given letter symbols and also names shown in table 2 to aid in discussion. Most of the fractions are actually heterogenous with respect to acid–base character.

Nitrogen Types

Total nitrogen value, N_T, was determined with a reductive, hydrogen–nickel pyrolysis tube followed by an ammonia microcoulometer cell. A cool boat inlet system was used. Nonaqueous potentiometric titration was used to classify the nitrogen compounds[12,13] into strong base nitrogen, N_{SB} (pKa > 8); weak base nitrogen, N_{WB} (pKa 8 to 2); very weak base nitrogen, N_{VWB} (pKa 2 to -2); and nonbasic nitrogen N_{NL} (pKa < -2). Examples of the various nitrogen compounds which fall in these basic types are: Strong base type (alkylamines), weak base type (pyridines, quinolines, anilines, highly ring alkylated pyrroles, N-methyl indoles, etc.), very weak base type [pyrroles, indoles, amides (including cyclic amides)], and nonbasic types (nitriles, carbazoles, second nitrogen atom in some diazo-compounds, etc.). Because some pyrroles and indoles titrate only about 70 percent, they contribute to the nonbasic nitrogen also. Infrared spectrometry of dilute solution absorption near 3,480 cm⁻¹ was used to determine pyrrolic NH type, nitrogen

N_{N-H}.[14,15] Colorimetry[16,17] was used to determine α- or β-unsubstituted pyrrolic-type nitrogen N_{pyr} (excludes carbazoles).

Oxygen Types

Infrared spectrometry of dilute solutions in the free −OH region was used to classify oxygen types based on the frequency of the absorption supplemented by the fractionation sequence information. In acid fractions 3,610 cm^{-1} was assumed specific for phenols and 3,530 cm^{-1} was assumed specific for carboxylic acids.[20,21] In fractions generated below A_3 in the sequence, the 3,610 cm^{-1} absorption was assumed to represent sterically hindered phenolic types which were not taken up by the anion-exchange resin. The 3,530 cm^{-1} region absorption for the post-acidic fractions was attributed to sterically hindered carboxylic-type compounds. Alcoholic OH, bridged phenolic OH, or some amide N−H absorptions would have been indistinguishable from that assigned to sterically hindered carboxylic OH. Spectra of the fractions were run at such dilution that Beer's law applied for the absorptions considered. Calibrations were made based on measured molar absorptivity values for the specific type compounds: Phenol and alkylated phenols, and octanoic and benzoic acids. The molar absorptivity for the sterically hindered OH-type calculations was assumed equal to that of the corresponding unhindered free OH.

RESULTS AND DISCUSSION

Distribution of Organic Material in Fractions

In table 2 the gravimetric recoveries of various fractions are compared for the two oils. The A_1 and A_2 acid fractions together represent about 3.2 percent of either oil. The AGRO fractionates equally between the two, but the ISRO is split with A_2:A_1 equal to 1.5. In the last acid fractions, A_3, the AGRO:ISRO ratio is 1.7. The quantities of base fractions are similar, as are those of the hydrocarbon fractions (N_0). The N_1, AGRO:ISRO ratio is 1.67 and the N_2 ratio is 3.5. Based on the data in table 2, the distillates show some differentiation in distribution of the very weak acid fractions. The AGRO distillate shows considerably more weak acid present than the ISRO distillate. The neutral fractions adsorbed by ferric chloride represent twice as much material in the AGRO as in the ISRO distillate. Basic and neutral hydrocarbon fractions are comparable in quantity for the two distillates.

Titrations

Distillates

The titration data for the two distillates and fractions as weight percent of the distillates are shown in table 3. Total nitrogen concentrations for the two oils are the same. The AGRO titration shows 0.79 percent N_{WB} compared to 0.90 percent N_{WB} for the ISRO. The N_{VWB} value in the AGRO is 0.42 percent compared to 0.22 percent in the ISRO. The AGRO oil shows slightly less N_N than the ISRO. In summary the titratable bases are similar in amount for the two distillates. The ratio AGRO:ISRO for N_{WB} is 0.88 and for N_{VWB} 1.9 indicating lower basicity--i.e., fewer weak bases and more very weak bases--for the AGRO although there is a slightly higher N_N value for the ISRO.

Acidic Fractions

The very weak acid fractions A_1 plus A_2 AGRO:ISRO, N_{VWB} ratio is 1.8 which is in the same direction as the similar ratio for the whole distillates. In the A_2 fractions the AGRO:ISRO, N_{VWB} ratio is 10 although the amount of base represented is small. Bases in the A_3 fractions are low in quantity and comparable.

TABLE 3. – Distribution of weakly basic, very weakly basic, and nonbasic
nitrogen in fractions and distillates

| | Nitrogen, wt-pct of light distillate | | | | | |
| | Aboveground | | | In situ | | |
Fraction	N_{WB}	N_{VWB}	N_N	N_{WB}	N_{VWB}	N_N
Distillate	0.79	0.42	0.13	0.90	0.22	0.22
A_1	.010	.056	.017	.009	.045	.023
A_2	.013	.031	.004	.015	.003	.007
A_3	.005	0	.005	.004	.001	.006
B_1	.016	.012	.005	.026	.006	.005
B_2	---	.009[a]	---	---	.005[a]	---
B_3	.59	0	.033	.72	0	.023
N_1	.014	.130	.056	.010[b]	.085	.034
N_2	.041	.057	.054	.013[b]	.019	.004
N_0	.001[b]	.074	.038	.002	.015	.070
	Recoveries					
Total in fractions[c]	.69	.37	.21	.80	.18	.17
Change in type	-.10	-.05	+.08	-.10	-.04	-.05

[a] Too small to titrate; this figure is based on the total nitrogen.
[b] Approaches strong-base titration characteristic potential.
[c] Total nitrogen recovery AGRO = 94 percent; ISRO = 86 percent.

Basic Fractions

In the two very weak base fractions, B_1 and B_2, the overall basicity of the bases titrated is less for the AGRO fractions as in the original distillates. The weak base fractions for both oils titrate almost completely as weak bases with an AGRO:ISRO N_{WB} ratio of 0.82. A small amount of nonbasic nitrogen is present.

Neutral Fractions

The amount of nitrogen in the three neutral fractions which titrate as weak base or very weak base is remarkable. The total nitrogen, N_T, in these fractions is 0.465 weight-percent of the AGRO and 0.252 percent of the ISRO. Based on an assumption of one nitrogen atom per molecule and a molecular weight in this distillate of about 200, these figures would represent 7 weight percent of the distillate as nitrogen-containing compounds retained by the ion-exchange resins for the AGRO and about 4 percent for the ISRO distillate. The potential for polymerization of pyrroles, and more slowly indoles, in acid media[22] and for their loss to cation-exchange resins[23] is well known so that the question of artifact formation of neutrals through polymerization was considered. Previous work[4] showed less than 0.5 weight percent polymer in neutrals from cation-exchange fractionation of the AGRO. Weak base titrations in this paper approaching strong base character were observed for the AGRO-N_0 fraction and for the ISRO-N_0 and N_2 fractions. Because no strong base titration is observed for the original distillates, this suggests possible pyrrole trimer formation which would have a strongly basic nitrogen atom in addition to two pyrrolic-type nitrogen atoms. The nitrogen and oxygen types observed in the neutral fractions are treated in the following discussion as the monomeric entities the functional parts would represent.

The summation of titrations on the AGRO fractions N_0, N_1, ond N_2 indicates them to contain about twice the basic nitrogen concentration of the ISRO neutrals. These levels represent about 26 percent of the basic nitrogen and 114 percent of the neutral nitrogen for the AGRO and about 13 percent of the basic and 49 percent of the neutral nitrogen for the ISRO.

The overall nitrogen recovery from table 3 was 94 percent for the AGRO, which is probably within the experimental error involved, but only 86 percent for the ISRO, which probably indicates a real loss of nitrogen-containing compounds to the columns. The oils showed similar decreases in N_{WB} and N_{VWB} as shown at the bottom of table 3, but the AGRO showed an apparent increase in N_N compared to a loss in the ISRO N_N. The increase in N_N for the AGRO could represent a shift in more basic nitrogen to nonbasic nitrogen. Since the shift is toward formation of neutral nitrogen, oxidation might be a suspected cause. Care was taken to prevent this by nitrogen purging. Another possible explanation is that titration characteristic potentials depend to some extent on the matrix os shown by Buell.[18] We assume the latter to be the case and that the net decrease in basic nitrogen and increase in N_N in the AGRO occurred for this reason.

In summary the distillates and fractions indicate that the AGRO has lower basicity in general than the ISRO. This is consistent with a picture of a more oxidized oil since, for example, oxidation of most amines produces weaker bases or nonbasic compounds. There was appreciable loss of nitrogen in the fractionation of the ISRO, but this was not so for the AGRO. Questions of artifacts possibly introduced by the separation scheme have not been thoroughly assessed but have been discounted in the following discussions.

Pyrrolic-Type Nitrogen

Table 4 shows the distribution of pyrrolic-type nitrogen in the oils and their fractions. The notable differences here are the larger N_{N-H} in the AGRO and the large loss from this category in the fractionation.

The loss of N_{N-H} is interpreted as follows. Because the initial values of pyrrolic-type nitrogen in the AGRO distillate are $N_{NH} = 0.21$ and $N_{pyr} = 0.11$, the latter value does not include 0.10 weight percent of the distillate which represents closely the loss of N_{N-H} through the fractionation sequence. All the other pyrrolic nitrogen values in the original oils are preserved in the fractions within experimental error. The observed loss of 0.10 weight-percent of the AGRO distillate os N_{N-H} represents a real difference between these oils. One type of material this could represent is carbazoles, but these are believed to be excluded by the distillate cut points.[4] Pyrroles or indoles with α and β substituents are an alternative interpretation fitting this boiling range.[4] Pyrroles are known to be lost rapidly to cation-exchange resins while indoles react at a much slower rate.[23] Based on these facts, the $N_{N-H} = 0.11$ weight-percent of the oil is postulated to represent α- and β-substituted pyrroles. Using this assumption that pyrroles have been lost to the cation-exchange resin and that the pyrrolic nitrogen remaining is indole type, the ratio of N-H pyrrole nitrogen to indole nitrogen in the AGRO would be about unity but for the ISRO the ratio would be about 0.23. The N_{pyr} values are largely recovered in the froction and probably represent mostly indole-type nitrogen assumed shown by the N_{N-H} values in the recovered fractions.

It might be expected that the higher temperature oil, the AGRO, would show N_{N-H} predominantly because as shown by Jacobson[24,25] N-alkyl pyrroles and indoles reorrange thermally to C-alkyl isomers. Other unknowns such as the contact of the in situ oil with minerals in the postretorting region could account for differences however. That highly substituted N-H type pyrroles appear to be last preferentially to the columns in this work is surprising because these types are the more stable with respect ta polymerization in acidic media.[22] This subject requires further investigation.

TABLE 4. – Distribution of pyrrolic-type nitrogen

| | Nitrogen, wt-pct of light distillate | | | |
| | Aboveground | | In situ | |
Fraction	N_{N-H}	N_{pyr}	N_{N-H}	N_{pyr}
Original light distillate	0.21	0.11	0.16	0.11
A_1	.013	.017	.042	.046
A_2	.0022	.0008	.0023	.0016
A_3	.0016	.0002	.0003	.0001
B_1	.0018	.0016	.0028	.0026
B_2	.0005	.0003	.0002	.0002
B_3	.0027	.0017	.0028	.0008
N_1	.078	.043	.056	.035
N_2	.0077	.0042	.0032	.0011
N_0	.0016	.014	.024	.0023
	Recoveries			
Total in fractions	.11	.083	.13	.090
Change in type	–.10	–.03	–.03	–.02

In the first acidic fractions, A_1, the AGRO shows about one-fourth of the N_{N-H} and one-third of the N_{pyr} that the ISRO fraction does. Both oils show concentration of N_{N-H} and N_{pyr} in the first neutral fraction. The AGRO N_0 fraction shows 6 times the N_{pyr} of the other oil, but the N_{N-H} values are reversed with the ISRO showing 15 times the AGRO N_{N-H} value.

Oxygen–Containing Types

Heteroatoms Per Molecule

Tables 5 and 6 show summaries of nitrogen types and hydroxylic types for the AGRO frac-tions and the ISRO fractions, respectively. The results are tabulated in milliequivalents per gram in the fraction. These numbers should be compared with a molal concentration of organic mate-rial of approximately 5 millimoles per gram for a distillate of M.W. 200 like the distillates we are discussing. The polar compounds in these distillates may be heavier than this but will not change the interpretation much. The total of nitrogen and oxygen atomic concentrations obser-ved runs as high as 6.36 in the fractions indicating an average of as much as 1.3 heteroatoms per molecule in some cases. The oils appear similar in respect to the heteroatom–per–molecule values based only on nitrogen and hydroxylic oxygen.

Acid Fractions

The oils differ markedly in their hydroxylic composition in the acid fractions. It was ex-pected from the character of the anion-exchange resin that most of the phenols would be desorbed in the first two fractions, A_1 and A_2, and any carboxylic acids would appear in A_3. For the AGRO this appears true. Except for a minor amount of phenolic type in A_3, the fraction is carboxylic acid types. On the other hand for the ISRO, A_3 contains largely phenolic types with a minor amount of carboxylic types. The appearance of major amounts of phenolic types in A_3 for the ISRO suggests these phenolic types have electron-withdrawing substituents present to enhance their acidity. Substituents[20] which could produce considerable enhancement of the acidity of phenols are for example formyl-, cyano-, or nitro- although no identification of these types of

TABLE 5. - Nitrogen and oxygen types in an aboveground, combustion retorted light distillate

Fraction	Wt-pct of oil	Heteroatomic type, milliequivalents per gram of fraction						Phenolic -OH	Carboxylic -OH	Total -OH$_T$	Total N$_T$ + OH$_T$
		N_{WB}	N_{VWB}	N_N	N_T	N_{N-H}	N_{pyr}				
A_1	1.65	0.42	2.42	0.73	3.57	0.58	0.77	2.50	0.13	2.63	6.20
A_2	1.60	.60	1.39	.20	2.19	.10	.037	3.99	.19	4.18	6.36
A_3	1.32	.29	0	.28	.57	.091	.013	.91	2.42	3.33	3.90
B_1	.48	2.35	1.82^b	.69	4.86	.28	.25	.04	.06	.10	4.96
B_2	.11	-	5.52^b	-	5.52	.31	.19	.03	0	.03	5.55
B_3	8.45	4.98	0	.28	5.26	.024	.015	.01	0	.01	5.27
N_1	4.75	.21	1.99	.84	3.04	1.21	.66	.57	.02	.59	3.63
N_2	2.20	1.32	1.84	1.74	3.99	.26	.14	.04	.07	.11	4.10
N_0	79.44	.0007	.065	.034	.10	.001	.013	0	0	0	.10

^{a}Partially soluble. ^{b}Not titrated because of small size of fraction.

TABLE 6. - Nitrogen and oxygen types in an in situ combustion retorted light distillate

Fraction	Wt-pct of oil	Heteroatomic type, milliequivalents per gram of fraction						Phenolic -OH	Carboxylic -OH	Total -OH$_T$	Total N$_T$ + OH$_T$
		N_{WB}	N_{VWB}	N_N	N_T	N_{N-H}	N_{pyr}				
A_1	1.32	0.50	2.43	1.26	4.19	2.29	2.51	1.45	0.058	1.51	5.70
A_2	1.87	.56	.13	.25	.944	.089	.061	4.89	.109	5.00	5.94
A_3	.76	.34	.084	.006	.430	.031	.014	5.02	.715	5.74	6.17
B_1	.57	3.31	.72^b	.69	4.72	.36	.33	.08	.02	.10	4.82
B_2	.08	-	4.21^b	-	4.21	.21	.19	.86	.05	.91	5.12
B_3	10.12	5.11	0	.16	5.27	.020	.006	.01	0	.01	5.28
N_1	2.84	.26	2.15	.86	3.27	1.43	.89	.09	.03	.12	3.39
N_2	.63	1.46	2.14	.48	4.08	.37	.12	.08	.02	.10	4.18
N_0	81.85	.002	.013	.061	.076	.021	.002	0	0	0	.08

^{a}Partially soluble. ^{b}Not titrated because of small size of fraction.

materials has been made in shale oils. The phenolic:carboxylic molal ratios are about 4 for the AGRO and about 16 for the ISRO. The A_3 fractions were of limited solubility in carbon tetrachloride so that the actual acid concentrations may have been larger than observed. If fraction AGRO, A_3 were presumed to be 100 percent carboxylic acids plus phenols, the phenolic:carboxylic ratio could be as low as 3. Higher N_N in the ISRO-A_1 fraction correlates with the greater pyrrolic nitrogen-type values observed in table 4. The N_{VWB} for the AGRO-A_2 fractions is 10 times that for the other oil. It does not correlate with N-H so this material may be amide type, including cyclic amide (pyridone, quinolone, etc.) types which have been indicated before.[4] Additional neutral nitrogen in the AGRO-A_3 fraction could also be placed in this category for the same reasons.

Base Fractions

Small amounts of hydroxyl appear in the base fractions and are comparable for the oils except in the B_2 fractions. This fraction of either oil is such a small amount of the oil it will not be discussed further.

Neutral Fractions

No hydroxyl absorption appeared in the N_0 (hydrocarbon) fractions. The AGRO-N_1 fraction shows six times the hydroxyl absorption that the ISRO-N_1 fraction does. In addition, the AGRO-N_1 fraction is 4.75 weight-percent of the oil whereas the ISRO-N_1 fraction is 2.84 weight-percent of its oil. The AGRO-N_1 fraction represents a much larger hydroxyl concentration in the oil than the ISRO-N_1 fraction. The AGRO-N_2 fraction is 2.20 weight-percent of its oil and the ISRO-N_2 fraction is only 0.63 percent of its oil although it has slightly higher -OH concentration. The summation of hydroxyl types in the neutral fractions gives a molar ratio AGRO:ISRO of 9 in the oils with the concentration of these hydroxylic neutral types in the AGRO being only 0.03 milliequivalent/gram oil.

In the neutral fractions, nitrogen-containing types appear much more abundant than hydroxyl types. From the AGRO neutral fractions the summation of nitrogen concentrations is 0.31 meq/g oil and from the ISRO neutral fractions the nitrogen concentration is 0.18 meq/g oil either of which is over an order of magnitude above the hydroxyl-type concentrations found in either.

Nonhydroxylic Oxygen Types

The comparison of the concentrations in the distillates of each of the heteroatoms S, N, and O is shown in table 7 along with O-phenolic, O-carboxylic, and N_{VWB} found in this work. The value of phenolic plus carboxylic oxygen in the AGRO = 0.23 and in the ISRO = 0.17. This is about 77 percent of the ISRO distillate total oxygen but only about 30 percent of the AGRO distillate oxygen. Assuming N_{VWB} to contain one oxygen atom per molecule and including it in the summation of oxygen types would account for 150 percent of the ISRO distillate oxygen but only 70 percent of the AGRO distillate oxygen. This suggests a large portion of the oxygen in the AGRO occurs in other forms than we have considered. Dinneen[5] has shown the presence of benzofuran in an AGRO-type naphtha and perhaps these types occur in this distillate also. Combinations of oxygen with sulfur could also account for the rest of the oxygen. Previous examination[4] of the AGRO showed sulfoxides absent but other forms were not determined.

CONCLUSIONS

This paper shows that there can be considerable variation in the distribution of some nitrogen and oxygen types in two combustion retorted shale oils. It is not presently possible to infer

TABLE 7. – Comparison of heteroatomic types in 400 to 600° F distillate fractions

Species	Concentration in distillate, meq/g	
	Aboveground	In situ
S_T	0.28	0.17
N_T	.96	.96
O_T	.78	.22
Oxygen Accounted For		
O_T		
O-phenolic	.15	.15
O-carboxylic	.08	.02
N_{VWB}	.30	.16
Total	.53	.33

much about retorting mechanism from these data because of the many unknowns in the post-retorting regions in the production of the oils. The analyses of these two oils show many qualitative differences in polar fractions which could form the basis for a retorting index or parameter for comparative evaluation of shale oils.

SUMMARY

The differences in observed chemical types for the AGRO and ISRO could be interpreted largely in terms of a greater oxygen content in the AGRO. Part of this oxygen in the AGRO may be showing up as higher very weak base content (probably amides) compared to the ISRO distillate. The molal ratio of weak bases AGRO:ISRO is 0.88 and the ratio of very weak bases AGRO:ISRO is 1.9. The AGRO pyrrole:indole ratio calculated is unity, but the ISRO pyrrole:indole ratio is 0.23. The molal ratio of phenolic:carboxylic acids is about 5 for the AGRO but about 16 for the ISRO. Small amounts of hydroxyl occur in the neutral nitrogen fractions of the oils but are dwarfed by the nitrogen content. The nonhydrocarbon neutral fractions of the AGRO represent twice the concentration in the oil that the similar ISRO neutral fractions do. Hydrocarbon fractions from both oils show appreciable (0.3 to 0.5 percent) pyrrolic nitrogen concentrations. To account for the oxygen level in the AGRO, oxygen types other than hydroxylic, carboxylic, and amidic must be considered to account for 30 percent of the AGRO oxygen, but the ISRO oxygen could be accounted for this way. Although marked differences in the oils can be observed, conclusions about differences in retorting based on the heterocompound types found are tenuous because of the many questions involved in the post-retorting history of the oils.

ACKNOWLEDGMENT

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